

and Oils in Industry

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For a long time we have used inedible animal fats and oils and products made from them in a wide variety of industrial applications, many of which have been modified only a little since they were first developed.

But now the industry is entering an era of expansion and development, comparable to periods passed through by both the petroleum and coal-tar industries, in which emphasis is being placed on isolating and preparing chemically homogeneous substances.

This approach opens a tremendous field for fundamental and applied research and for the manufacture of many new products. Such a trend promises increased income to the farmer, industrialist, and wage earner, as well as many products to add to the public comfort and health.

As industrial raw materials, it is the inedible grades of animal fats and oils that are used almost exclusively. Inedible tallow and grease comprise about 90 percent of these materials, with pork fat and neatsfoot oil making up the rest. Factory consumption of inedible animal fats and oils in 1947 to 1950 was about 2 billion pounds a year.

Inedible tallow comes mostly from cattle and sheep as trimmings from meat-packing plants or as scrap fats obtained from meat trimmings in butcher shops or saved in the kitchen and sold to commercial renderers for processing. A large amount of inedible

pork fat is marketed as grease, an average of about 5 pounds of grease being produced for each hog slaughtered. Other sources of grease are city garbage, waste fat from restaurants and hotels, and bones. When production of lard exceeds the demand, a part of this edible fat is diverted to grease.

Although grease is ordinarily considered to be hog fat, and tallow the fat of cattle and sheep, the commercial distinction between greases and tallows is made entirely on the basis of the titer (the temperature at which solidification occurs) of the fatty acids obtained from the fat. If the titer is below 40° C., the fat is a grease; above 40° C., the fat is a tallow.

Inedible tallows and greases are graded on the basis of color, content of free fatty acids, and general quality—flavor and odor. The important grades of tallow, in order of quality, are: Prime (Packers') Tallow, produced from the choicest inedible stock; Number One Tallow, the most widely used industrial grade; and Number Two Tallow. The important grades of grease are A White Grease, B White Grease, Yellow Grease, and Brown Grease.

For most uses, the materials have to be modified chemically. The only important exception is neatsfoot oil, which is prepared from the feet and shinbones of cattle and is used in lubricants and dressings for leather. Only 3 million to 4 million pounds of neatsfoot oil is produced annually, a relatively small percentage of the total quantity of inedible animal fats consumed by industry.

The most important outlet for inedible animal fats is in making soap, a chemical process that has been conducted for hundreds of years and for a long time was almost the only outlet for inedible animal fats. Soap accounts for about 80 percent of the inedible

animal fats, or about 1.5 billion pounds (1943 to 1950), consumed in the United States annually. Saponification of fats with alkali yields glycerol as well as soap.

Some of the many uses of glycerol are in the preparation of explosives and synthetic resins, as a moistening agent, and in the food, cosmetic, and pharmaceutical industries.

Everybody uses soap because of its detergent properties. Soap is an excellent detergent in soft water and at an alkalinity greater than pH 8, but not in hard water. For use where water is hard, synthetic detergents, which are said to be equal or superior to soap, are now available, the result of intensive industrial research. The production and consumption of synthetic detergents have increased tremendously and will probably continue as new uses for these products, based on certain of their properties, are found.

The production and consumption of soap have remained substantially constant (1943 through 1949), despite the active competition from the newer detergents in a field that until recently was reserved almost exclusively for fat derivatives. The use of inedible fats in the preparation of synthetic detergents is increasing, but chemicals from petroleum and coal tar are still by far the most important source materials in synthetic-detergent manufacture. Production of synthetic detergents was about 300 million pounds in 1947, 500 million in 1948, 800 million in 1949, and about 1 billion in 1950.

Another important industrial outlet for inedible animal fats and oils is in the preparation of lubricants and lubricating greases, which account for somewhat less than 5 percent of the annual consumption, or approximately 100 million pounds.

Most of the remaining inedible animal fats and oils (10 to 15 percent of the total, or 200 million to 300 million pounds) go into the preparation of free fatty acids, of which about 50 percent are used in the preparation of stearic acid and red oil. The remainder

are used in the preparation of soap (10 to 20 percent), lubricants and greases (about 10 percent), rubber, and miscellaneous products.

Minor applications for inedible animal fats and oils (5 percent of the total, or about 100 million pounds) are in the manufacture of synthetic detergents, leather, illuminating oils, cutting oils for metal-working operations, printing inks, and paints and varnishes.

Although most inedible animal fats and oils are converted by simple procedures to end products, which are then used up (soap, lubricants, greases), the fatty acids represent an intermediate stage in the consumption of inedible animal fats and oils, and find their way into a surprisingly wide variety of products.

FREE FATTY ACIDS obtained by hydrolysis of inedible tallow and grease consist of 40 to 50 percent saturated acids (mainly palmitic and stearic acids), as much as 10 percent polyunsaturated acids (mainly linoleic acid), and 40 to 45 percent of oleic acid, the monounsaturated acid. For many years this mixture was separated into solid and liquid fractions by pressing, to yield so-called stearic acid, originally employed in the preparation of candles, and red oil (or commercial oleic acid), originally considered to be of little value and occasionally discarded or burned.

Commercial stearic acid consists of about equal parts of stearic and palmitic acids and it is contaminated with unsaturated acids, depending on the number and efficiency of the pressing operations. Thus, the terms single-, double-, and triple-pressed grades of stearic acid were introduced, the last-named containing the smallest proportion of unsaturated acids, occasionally as little as 2 percent, and having the highest melting point and the best color, odor, and stability to oxidation.

Red oil, or commercial oleic acid, is a yellow to dark-brown liquid that contains 60 to 75 percent oleic acid. The remainder is saturated and poly-

unsaturated acids in about equal quantities. Because of this composition, the conventional analytical values for red oil agree with those calculated for pure oleic acid. Many investigators thus assumed that red oil was chemically homogeneous. As a result, a great deal of research with red oil, rather than purified oleic acid, as the starting material has led to erroneous conclusions. By redistillation, the color of commercial oleic acid can be improved, but, because the composition remains almost the same, its stability of color and odor and resistance to oxidation are only slightly improved. The residue from this and other distillation operations in the preparation of fatty acids is called fatty acid pitch, or stearine pitch. It is used in electrical-insulating and roofing materials and in other materials that require a product with pitchlike properties.

Separation of solid- and liquid-acid fractions by pressing is mainly a hand operation. The process is slow, and labor costs are high. Other disadvantages are limitations in the quantity of fatty acids that can be separated, excessive product losses due to handling, and cost of remelting, chilling, repressing, and recycling. About 1945, however, a commercial solvent-crystallization process, the Emersol process, was developed for the separation of the solid from the liquid acids. The process separates the acids efficiently and it is continuous. Operating costs are said to be only about 35 percent of those for pressing. The composition of the solid and liquid fractions is about the same as that obtained by pressing. Because the process is efficient, the iodine number of the solid-acid fraction can be easily reduced below the value usually obtained by conventional cold- and hot-pressing operations.

Despite this lack of chemical homogeneity, the fatty acid fractions obtained by pressing or crystallizing operations have a good industrial position. Their use is widespread and increasing. The use of fatty acids in organic synthesis, however, can be ex-

pected to increase greatly when pure individual fatty acids are available.

The most important use for stearic acid is in compounding rubber. About 15 million pounds were used in 1949, out of a total of about 50 million pounds of stearic acid consumed. Stearic acid is also used in cosmetics, ointments, and shaving creams and in other pharmaceutical and toilet preparations. As shown by the number of pounds used in 1949 (in parentheses), it was used largely in the form of soaps (6 million), lubricants and greases (4 million), chemicals (7 million), candles (3 million), paints, varnishes, and resins (1.5 million), metal-working operations (1 million), textiles (1.5 million), and many miscellaneous applications (11 million).

Approximately 45 million pounds of commercial oleic acid were consumed in 1949. About 16 million pounds of that amount went into liquid, or low-melting, soaps intended primarily for use in textile-scouring operations. Commercial oleic acid is also used as a textile lubricant (10 million pounds), in the manufacture of chemicals (8 million), in lubricants and greases (2.5 million), sulfonated oils (3 million), rubber (1.5 million), protective coatings (1 million), resins (1 million), metal-working operations (1.5 million), and many miscellaneous industrial applications.

The instability of color and odor of commercial oleic acid and the ease with which it forms gummy polymerization and oxidation products are serious drawbacks to many industrial uses. It has been impossible to eliminate the disadvantages by the use of inhibitors or antioxidants. The undesirable characteristics can be attributed to the high percentages of polyunsaturated acids in the commercial product, which oxidize and polymerize faster than oleic acid. Textiles lubricated with red oil and stored for long periods may burst into flame as a result of spontaneous combustion, caused by the evolution of heat during oxidation of the polyunsaturated acids. The gummy de-

posits formed on textiles lubricated with red oil cannot be removed by scouring and may cause uneven dyeing and unpleasant odors in the finished fabric.

Commercial oleic acid is not a good chemical intermediate, because the impurities, notably polyunsaturated acids, cause reactions to proceed inefficiently and result in low yields. It is difficult—sometimes impossible—to isolate a desired derivative in a pure state. Purified oleic acid is a much better intermediate from the dollar-and-cents standpoint. The polyunsaturated acids, which react much as oleic acid does, require the use of enough chemicals to react with all the unsaturated components present, because preferential reactions are usually not available.

The earliest procedure for separating the saturated and polyunsaturated acids from oleic acid consisted in fractional crystallization of the soaps of the mixed acids from organic solvents. With proper selection of soap and solvent, the oleic acid could be purified at convenient operating temperatures on a small laboratory scale, but such procedures were tedious and unsatisfactory on a larger scale. In general, procedures involving crystallization of soaps have been abandoned.

As the polyunsaturated acids are more soluble and the saturated acids are less soluble in organic solvents than oleic acid, procedures have been developed for the solvent crystallization of mixed fatty acids. The procedures are workable even on a large laboratory scale, but crystallization temperatures in the range of -50° to -70° C. are required. Those temperatures are not readily attainable industrially at present, and many engineering problems are introduced. Furthermore, the solvent action of the polyunsaturated acids on oleic acid causes loss of oleic acid with the polyunsaturated acids, and even interferes with separation of the saturated acids.

THE FIRST commercially feasible procedure for the preparation of puri-

fied oleic acid (oleic acid content 90 to 98 percent) was described in a preliminary report by Daniel Swern and John T. Scanlan, of the Eastern Regional Research Laboratory, in 1944. Complete details of this procedure were published in 1946; in 1948 a public service patent (U. S. 2,457,611, assigned to the Secretary of Agriculture) on this process was granted to Dr. Swern and Waldo C. Ault. Nonexclusive licenses to operate under the patent can be obtained without cost from the Secretary of Agriculture.

Inedible tallow or grease is the starting material. Most of the polyunsaturated acids (in the form of glycerides) are first converted to monounsaturated acids (in the form of glycerides) by selective hydrogenation. Hydrolysis of the selectively hydrogenated fat gives a fatty acid mixture, consisting mainly of saturated and monounsaturated acids. By solvent crystallization of the mixed acids at temperatures from 0° to -20° C.—temperatures well within the operating range of present-day commercial practice—the solid acids precipitate and are easily separated by filtration. The solid acids, corresponding to the double-pressed grade, are obtained in good yield. Recovery of the solvent from the filtrate yields a residue consisting of 90 percent oleic acid, 1 to 3 percent polyunsaturated acids, and saturated acids. By fractional distillation, the oleic acid content can be raised to 98 percent. Pilot-plant and cost-evaluation studies indicate that the purified oleic acid should cost only slightly more than red oil. The process was placed in large-scale commercial operation in 1949.

Another development in the preparation of a purified grade of oleic acid is the process of Emery Industries, Inc. It consists in preferential polymerization of the polyunsaturated acids in red oil to a nonvolatile dimer, from which the more volatile oleic acid is separated by distillation. A basic difference between the preferential polymerization process and the selective-hydrogenation process is that in the former the

starting material is red oil, which is a partially fractionated or purified product already, whereas in the latter the inedible fat is the starting material, and only one fractionation procedure to obtain purified oleic acid is employed.

Purified oleic acid can be used directly wherever stability in color and odor and high resistance to oxidation and polymerization are required, and as a chemical intermediate. The disadvantages caused by polyunsaturated acids are largely eliminated. In some applications, however, low melting point and resistance to solidification of the products (soaps, greases) are more important than chemical homogeneity, and for such uses, red oil, which usually has a lower melting point than purified oleic acid, will probably always be in demand. Some degree of chemical homogeneity is attained, however, even with the present commercial grades of fatty acids, as they are monobasic, long-chain aliphatic acids.

Because oleic acid contains two reactive functional groups, the carboxyl group and the carbon-to-carbon double bond, it undergoes numerous chemical reactions that yield potentially useful products. Reaction of the carboxyl group with appropriate reagents gives a wide variety of esters, amides, and salts (soaps). Alkyl esters of oleic acid can be used as plasticizers and textile lubricants, and alkenyl esters, such as the vinyl and chloroallyl, can be polymerized. The alkenyl esters can also be copolymerized with some commercially useful monomers, yielding copolymers ranging from glasses to rubbers. Because the long fatty chain is a part of the polymer molecule, modification in properties caused by the oleate is permanent. Generally, mechanical mixing of fatty derivatives with high-molecular-weight polymers is not satisfactory because the long-chain fatty compounds are not compatible with many industrially important polymers. Purified grades of oleic acid also show promise in the preparation of a synthetic, inedible substitute for olive oil.

Amides of oleic acid can be readily

converted to products with useful wetting and detergent properties. Soaps of oleic acid are useful in the preparation of oxidation catalysts and high-quality, stable greases. Water-soluble soaps of oleic acid can be used as emulsifying agents in low-temperature polymerization reactions, because they neither inhibit the reaction nor precipitate. Selective hydrogenation of oleic acid, or reduction with sodium, yields oleyl alcohol, which undergoes a wide variety of interesting and useful reactions and is a good emulsifying agent.

Reaction of the double bond of oleic acid yields many products of potential and actual value, such as monohydroxystearic and dihydroxystearic acids, epoxystearic acids, arylstearic acids, and monobasic and dibasic acids by oxidative cleavage with oxygen. The preparation of those acids by cleavage of oleic acid with oxygen is one of the most important problems in the field of fats, because both fragments are immensely important in the preparation of plastics, plasticizers, and low-temperature lubricants, and as chemical intermediates. The epoxy and hydroxy acids are potentially useful intermediates in the preparation of plasticizers, wetting agents, and waxes; salts of the arylstearic acids are potentially useful addition agents to lubricants.

The carboxyl group of the saturated acids also undergoes the reactions discussed under oleic acid. The absence of the double bond, however, gives the molecule a stability that derivatives of oleic acid do not have. Amides, particularly those of the saturated acids, are well-established industrial products and are used to make wetting agents, waxes, and water repellents, and as chemical intermediates.

It is often rash—but always exciting and challenging—to make predictions. The development that appears to hold the most promise for the large-scale consumption of inedible animal fats and oils is the preparation of chemically homogeneous substances and their derivatives.

Most of the present uses for inedible

animal fats and oils do not require chemical homogeneity—in fact, homogeneity may sometimes be a disadvantage. But where mixtures are employed to obtain certain average properties, substitute materials that are less expensive, more readily available, or superior are always appearing on the market.

Every organic compound has its own special chemical and physical properties, as well as properties common to all members of its homologous series. Thus, compounds having long-chain molecules are high-boiling, water-insoluble, and relatively nonvolatile and water-repellent. Some of them also have the property of lubricating and of modifying and lowering the solidification point of materials with which they are mixed. Furthermore, by chemical reaction, the long chain can be introduced into a wide variety of organic molecules, permanently imparting these characteristics to the final product.

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WALDO C. AULT was born on a farm in Ohio and was educated at Ohio State University, where he received the doctor's degree in 1934. After 7 years in industrial research, he joined the staff of the Northern Regional Research Laboratory. Later he transferred to the Eastern Laboratory, where he has since served as head of the oil and fat division.

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Soybeans processed by solvent-extraction, screw-press, and hydraulic-press methods

Crop year	Methods						Total by years
	Screw press		Solvent extraction		Hydraulic		
	1,000 tons	Percent	1,000 tons	Percent	1,000 tons	Percent	
1936-37.....	423	68.4	82	13.2	114	18.4	619
1937-38.....	637	70.1	156	17.1	116	12.8	909
1938-39.....	967	72.2	214	16.0	158	11.8	1,339
1939-40.....	1,274	74.4	346	20.2	92	5.4	1,712
1940-41.....	1,426	74.2	444	23.1	52	2.7	1,922
1941-42.....	1,715	74.1	558	24.1	41	1.8	2,314
1942-43.....	2,531	63.2	654	16.3	819	20.5	4,004
1943-44.....	2,786	65.2	699	16.4	784	18.4	4,269
1944-45.....	3,246	70.5	919	20.0	437	9.5	4,602
1945-46.....	3,073	64.2	1,347	28.2	363	7.6	4,783
1946-47.....	3,262	63.9	1,357	26.6	488	9.5	5,107
1947-48.....	2,647	54.4	1,830	37.6	388	8.0	4,865
1948-49.....	3,048	55.3	2,186	39.6	281	5.1	5,515